

Performance characterization of rigid polyurethane foam with refined alkali lignin and modified alkali lignin

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Abstract: The two kinds of rigid polyurethane (PU) foams were prepared with respectively adding the refined alkali lignin and alkali lignin modified by 3-chloro-1,2-epoxypropane to be instead of 15% of the polyether glycol in weight. The indexes of mechanical performance, apparent density, thermal stability and aging resistance were separately tested for the prepared PU foams. The results show that the mechanical property, thermal insulation and thermal stability for PU foam with modified alkali lignin are excellent among two kinds of PU foams and control samples. The additions of the refined alkali lignin and modified alkali lignin to PU foam have little effect on the natural aging or heat aging resistance except for decreasing hot alkali resistance apparently. Additionally, the thermal conductivity of modified alkali lignin PU foam is lowest among two kinds of PU foams and control samples. The alkali lignin PU foam modified by 3-chloro-1,2-epoxypropane could be applied in the heat preservation field.

Keywords: refined alkali lignin; modified alkali lignin; rigid PU foam; mechanic performance; thermal stability

Introduction

The study on the rigid polyurethane (PU) foam is one of the most interesting foam fields in recent decades (Saha et al. 2008). Many kinds of rigid PU foams with different properties are widely used in construction industry, energy saving building and floating field (Modesti and Lorenzetti. 2002; Modesti et al. 2002). With the attention to the reduction of petroleum resources and the world environmental problems, however, the biodegradable polyurethane prepared by biomass, partially instead of polyol has aroused people's wide interests (Correa et al. 1996). Some researchers have studied how to synthesize PU foam by using modified starch and beeswax, but the price of these industrial raw materials is higher than that of the industrial lignin. The industrial lignin would have an obvious potential for using as the raw material of PU foam.

Lignin is an abundant and renewable biomaterial widespread

in plants. Industrial lignin, which is a byproduct of the paper industry, exists in the black liquor of the pulping industry. Addition of lignin in the application of polyurethane not only is an effective method in using renewable biomass energy, but also provides polyurethane with excellent mechanical, heat-resistant and compression performance and aging-resistant performance (Thring et al. 1997; Vanderlaan et al. 1998; Helena et al. 2007; Kabir et al. 2006; Han et al. 2008; De Sousa et al. 2007; Nihal et al. 2007; Fabrice et al. 2006; Taro et al. 2006). As a result, some current studies have been conducted on preparing lignin-based PU foams (Liu et al. 2001) for heat insulation, filling and water-proof with the refined alkali lignin (Wei et al. 2006; Liu et al. 2003). The objective of this study was to analyze mechanical performance, apparent density and thermal stability for experimental two kinds of rigid PU foams with the refined alkali lignin, alkali lignin modified by 3-chloro-1,2-epoxypropane and control sample without lignin.

Materials and methods

Refined alkali lignin and modified alkali lignin

The rough lignin from pulping and paper factory was mixed with water at the ratio of lignin to water (1: 3, w/w). The pH value of the mixture was adjusted to 13 or 14 with about 10% NaOH solution and the rough lignin was dissolved completely. After removing insoluble residue, the pH value of the filtrate was adjusted to 2 with 12% hydrochloric acid at 60°C. The sediment was obtained by filtering and was washed to neutral with distilled water. It was dried for 36 h at 45°C under vacuum, and then the refined alkali lignin was obtained.

After dissolving 5-g lignin in 4% NaOH solution of 50 mL in

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250-mL flask, 20-mL epichlorohydrin (3-chloro-1,2-epoxypropane) was added to the flask, and then the flask was warmed and kept at 80°C for 3 h in the water bath with stirring at moderate speed. Two grams of NaOH was transferred into the system every 10 min in the first hour. The total amount of adding NaOH was 10 g during the first hour. The pH value of thick brown liquid was adjusted to 2 with 38% HCl after reacting. After removing the unmodified lignin or low molecular lignin, washing off the 3-chloro-1,2-epoxypropane oligomer with benzene and neutralizing with distilled water, the modified alkali lignin was prepared after drying at 50°C in oven.

PU foams preparation

After premixing 20-g polyethylene glycol (molecular weight of 400), 0.25-g dimethyl silicone oil, 1.75-g n-pentane and 0.015-g triethylene diamine completely, the polymeric phenyl methane-diisocyanate (PAPI) (23 g) was transferred into the pre-mixture under vigorous stirring at room temperature and poured into the mold quickly. Control PU foam was achieved after laying up 6–8 s. The refined alkali lignin PU foam and modified alkali lignin PU foam were prepared by refined alkali lignin and modified alkali lignin, instead of 15% of the polyethylene glycol, respectively.

Performance analysis

The tensile strength, bending strength, impulsion strength and compressive strength for the prepared PU foams and control were separately tested according to the related China national standards (GB6343-86, GB8812-88, GB/T1043-93 and GB8813-88). The density of the three samples was determined according to China national standards (GB6346-86). The thermal conductivity of the samples was tested and analyzed following China national standards (GB3399). Foam sample was transferred into an aluminum pan, and then was placed into a heating chamber of the NETZSH DSC242. The Differential Scanning Calorimetry (DSC) curve was obtained at a heating rate of 10 °C/min from 30°C to 400°C in the ambient air.

For the experiment of natural aging, the average weight retention rates for samples of control PU foam, refined alkali lignin PU foam and modified alkali lignin PU foam were calculated after being buried in soil at depth of 40 cm for 60 days. The average weight retention rates of the three samples were determined after treating for 30 days in oven at 105°C for the experiment of heat aging. For the hot alkali resistance, the samples were dipped into the 10% NaOH at 80°C for 24 h in advance, and taken out for drying until constant weight. The average weight retention rate of the samples was separately measured under the constant weight.

Results and discussion

Mechanical performance

The mechanical performances of control sample, refined alkali

lignin PU foam and modified alkali lignin PU foam tested are shown in Table 1. Although the mechanical performances of the lignin-based PU foam were lower than that of control sample except bending strength, the compressive strength is currently more than 0.3 MPa of compressive strength in the industrial standard. Therefore, the lignin-based PU foam still could be regarded as a kind of materials in industrial rank. Additionally, the bending strength of the lignin-based PU foam was higher than that of control sample. All the mechanical performances of the modified alkali lignin PU foam with 3-chloro-1,2-epoxypropane were better than those of the refined alkali lignin PU foam. The bending strength of modified alkali lignin PU foam was about 2 times that of refined alkali lignin PU foam due to the cross linking between lignin and 3-chloro-1,2-epoxypropane. After cross linking, the molecular weight of lignin-based epoxy resin increased and its stiffness became stronger so that bending strength of modified alkali lignin PU foam increased rapidly.

Table 1. The mechanical performances of Refined alkali lignin PU foam and Modified alkali lignin PU foam

Sample	Tensile strength (Mpa)	Compressive strength (Mpa)	Implusion strength (kJ·m ⁻²)	Bending strength (Mpa)
Control sample	1.040(6)	0.939(4)	3.015(6)	0.156(5)
Refined alkali lignin PU foam	0.593(6)	0.410(4)	0.912(6)	0.250(5)
Modified alkali lignin PU foam	0.634(6)	0.498(4)	0.965(6)	0.516(5)

Note: The number in parentheses is repetition times.

The mechanical performances of the prepared lignin-based PU foams in the experiments were better than those of the common rigid PU foam. This implies that two kinds of lignin-based PU foams have potential application prospect.

Apparent density and thermal conductivity

The apparent density and thermal conductivity of control sample, refined alkali lignin PU foam and modified alkali lignin PU foam were determined and the data are shown in Table 2.

Table 2. Apparent density and thermal conductivity for three kinds of samples

Sample	Apparent density (kg·m ⁻³)	Thermal conductivity (W·mK ⁻¹)
Control sample	148.90	0.014
Refined alkali lignin PU foam	79.50	0.012
Modified alkali lignin PU foam	110.37	0.010

The apparent densities of the three samples were in the range from 79.50 kg·m⁻³ to 148.90 kg·m⁻³, which are suitable for industrial production requirements between the media- and high-density polyurethane foams. The apparent density of modi-

fied alkali lignin PU foam was higher than that of the refined alkali lignin PU foam. Furthermore, the thermal conductivity of modified alkali lignin PU foam was the lowest among the three kinds of samples, indicating that the lignin PU Foam modified by 3-chloro-1,2-epoxypropane could be better applied in the heat preservation field. Generally, the thermal conductivities of the three kinds of synthesized PU foams were less than $0.033 \text{ W} \cdot \text{mK}^{-1}$ of the commercial PU foam, which can be used in the

heat preservation area.

Analysis of Differential Scanning Calorimetry (DSC) curve

Being one of the basic research tools, DSC has widely used in routine test in polymer materials. Glass transition behaviours and exothermic peaks of the samples were investigated by DSC (Fig. 1).

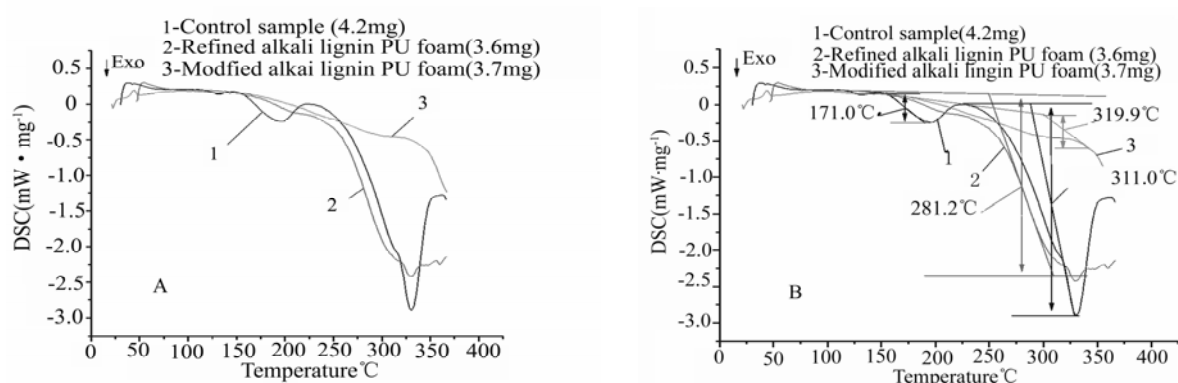


Fig. 1 DSC curves of the three samples

A----The whole DSC curves; B----The DSC curves with T_g

As shown in Fig. 1a and 1b, two exothermic peaks of the control sample can be found at about 190°C and 330°C , which indicates that polyurethane foam without lignin is not stable at relative temperature. The glass transition temperature (T_g) of the control sample is at 171°C and 311.0°C . For refined alkali lignin PU foam and modified alkali lignin PU foam, T_g is separately at 281.2°C and 319.9°C , which indicates that polyol in the residue started to decompose and carbon dioxide and some gaseous substances are released. Additionally, it is induced that the modified alkali lignin PU foam could be applied in heat resistant field due to its higher T_g .

The refined alkali lignin PU foam and modified alkali lignin PU foam that have one glass transition temperature generally indicated that the prepared foam was a homogeneous system in which lignin in polyurethane foam was cross-linked with PAPI rather than simply mixed. The modified alkali lignin PU foam had the best thermal stability among the prepared foams, followed by refined alkali lignin PU foam in heat resistance. The reason probably is that the refined alkali lignin could not react with PAPI sufficiently. The modified alkali lignin had much more functional groups than those of refined alkali lignin.

Aging

PU foam has the characteristic of aging resistance and the lignin is hard to be decomposed. The aging resistance was investigated in the experiments. The differences of weight retention rates between natural aging and heat aging resistances for three polyurethane foams are not obvious (Table 3). All the samples have very high age-resistant properties, indicating that the addition of the lignin has little effect on the natural aging properties or

heat-resistant properties except the alkaline-resistant properties. The natural aging and heat aging resistance of modified alkali lignin PU foam is better than that of refined alkali PU foam. This implies that the modified lignin is more stable than the refined alkali lignin for aging resistance. Addition of lignin decreased the alkaline-resistant properties of the PU foam. The lignin can be dissolved in alkali. The reactive ability and hydroxyl value of the lignin will increase after modifying by 3-chloro-1,2-epoxypropane. The adding ratio of lignin is restricted to some extent in the preparation.

Table 3. Weight retention rates of refined alkali lignin PU foam and Modified alkali lignin PU foam

Sample	Natural aging (%)	Heat aging (%)	Hot alkali aging (%)
Control sample	99.81	99.97	88.7
Refined alkali lignin PU foam	99.73	99.65	67.0
Modified alkali lignin PU foam	99.84	99.90	33.1

Conclusion

The lignin-based rigid polyurethane (PU) foams were prepared by separately adding the refined alkali lignin and alkali lignin modified by 3-chloro-1,2-epoxypropane to be instead of 15% of the polyether glycol in weight. The control sample was prepared without adding lignin. The mechanical performances of the prepared PU foams in the experiments were better than those of the commercial PU foam. Although the mechanical performances of the lignin-based PU foam were lower than that of the control sample except the bending strength, the compressive strength

was more than 0.3MPa of compressive strength in the industrial rank. All kinds of mechanical performances of the lignin PU foam modified by 3-chloro-1,2-epoxypropane were better than those of the refined alkali lignin PU foam.

The apparent density of modified alkali lignin PU foam was higher than that of the refined alkali lignin PU foam. Furthermore, the thermal conductivity of modified alkali lignin PU foam is the lowest among the three kinds of samples, indicating that the lignin PU foam modified by 3-chloro-1,2-epoxypropane could be better applied in the heat preservation field. Generally, the thermal conductivities of the three kinds of synthesized PU foams were less than that of the commercial PU foam.

The control sample had two glass transition temperatures, while the refined alkali and modified alkali lignin PU foams only had one T_g . Especially, the lignin PU foam modified by 3-chloro-1,2-epoxypropane had the highest T_g among the three samples, indicating that it had a better thermal stability and could be applied in the heat resistant field.

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